

## Electronic supplementary information (ESI)

$^1\text{H}$  NMR spectra of complexes **1–3** and their respective free ligands in  $\text{DMSO-d}_6$ . Logarithmic plots of observed first-order rate constants for BNPP cleavage by complex **2**. Biphasic kinetic curve for BNPP hydrolysis in the presence of **2**.

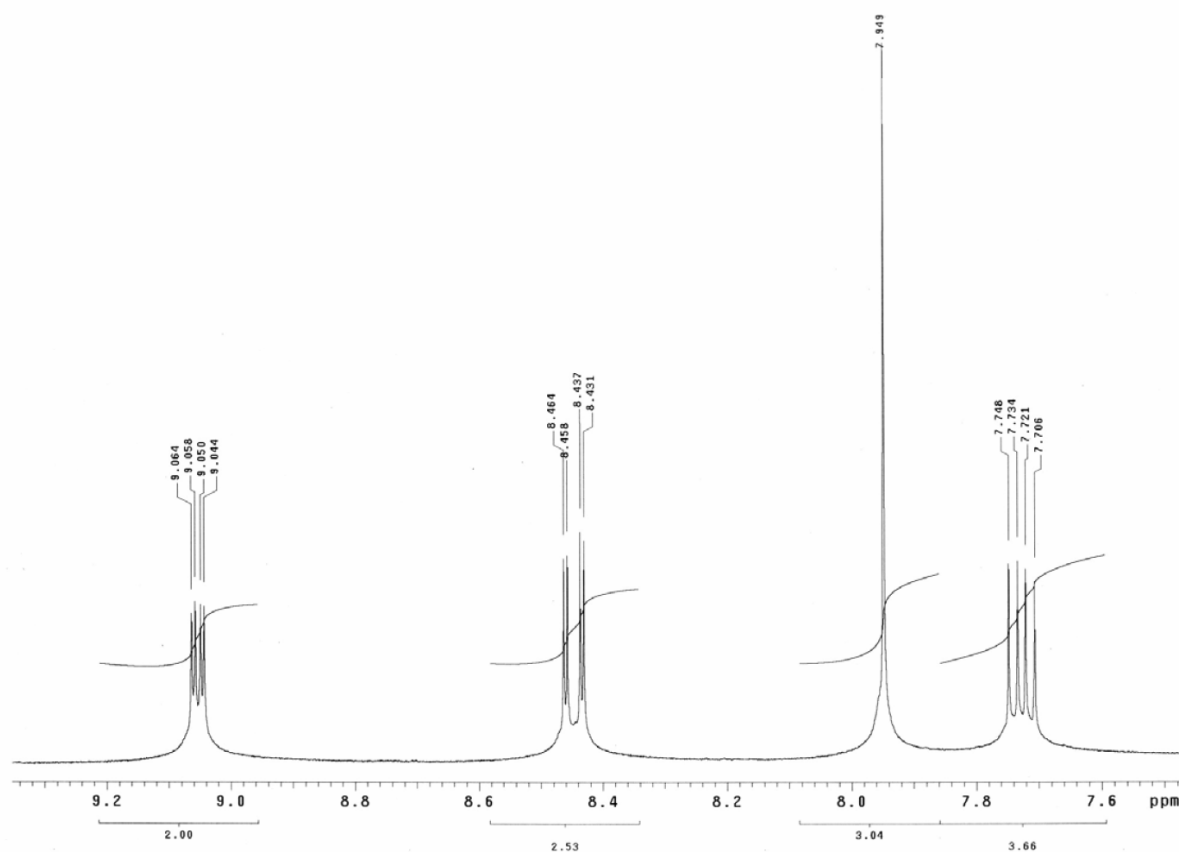


Fig. 1S.  $^1\text{H}$  NMR spectrum of 0.1 M phenanthroline in  $\text{DMSO-d}_6$

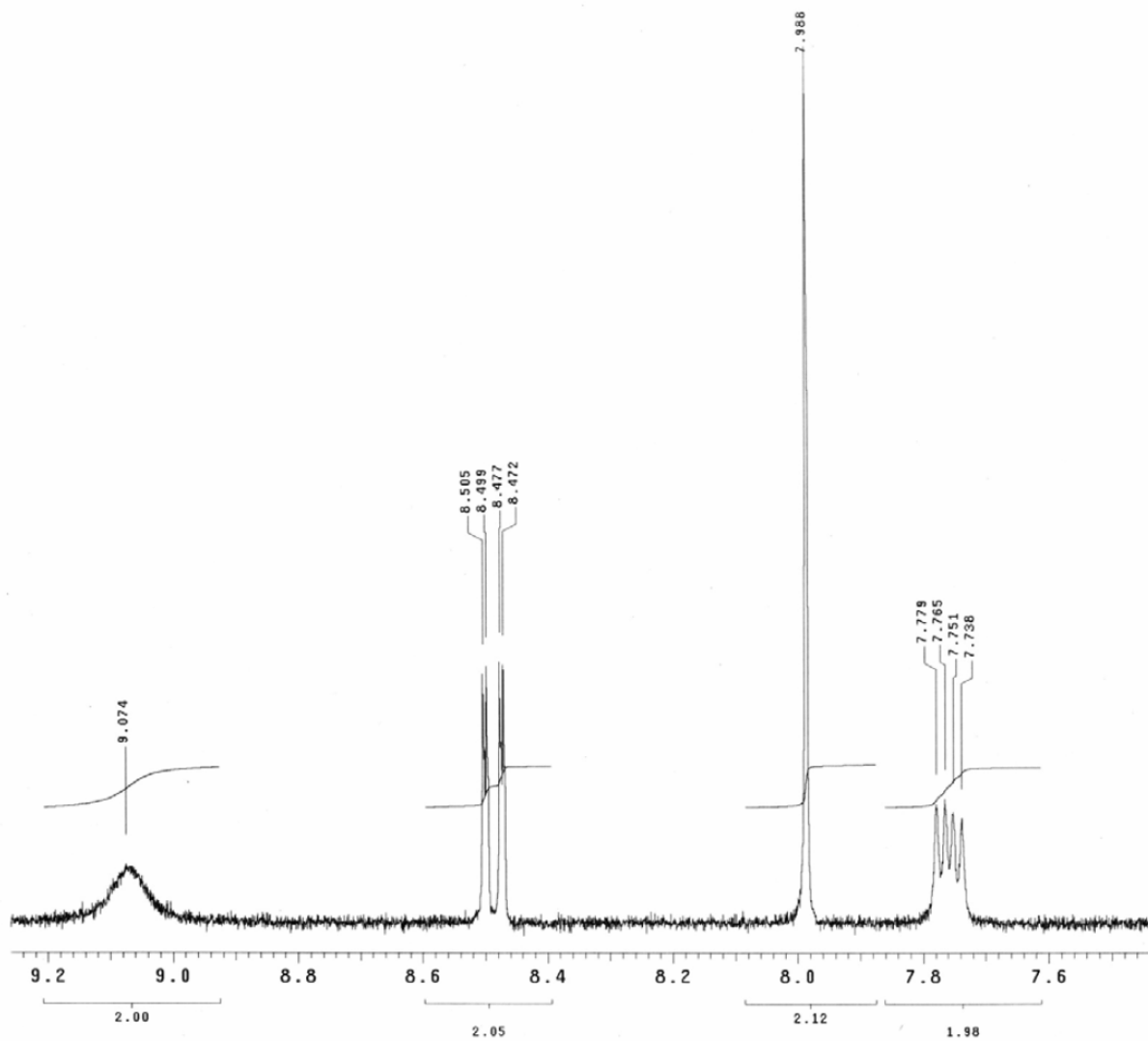


Fig.2S.  $^1\text{H}$  NMR spectrum of 0.05 M 1 in  $\text{DMSO-d}_6$

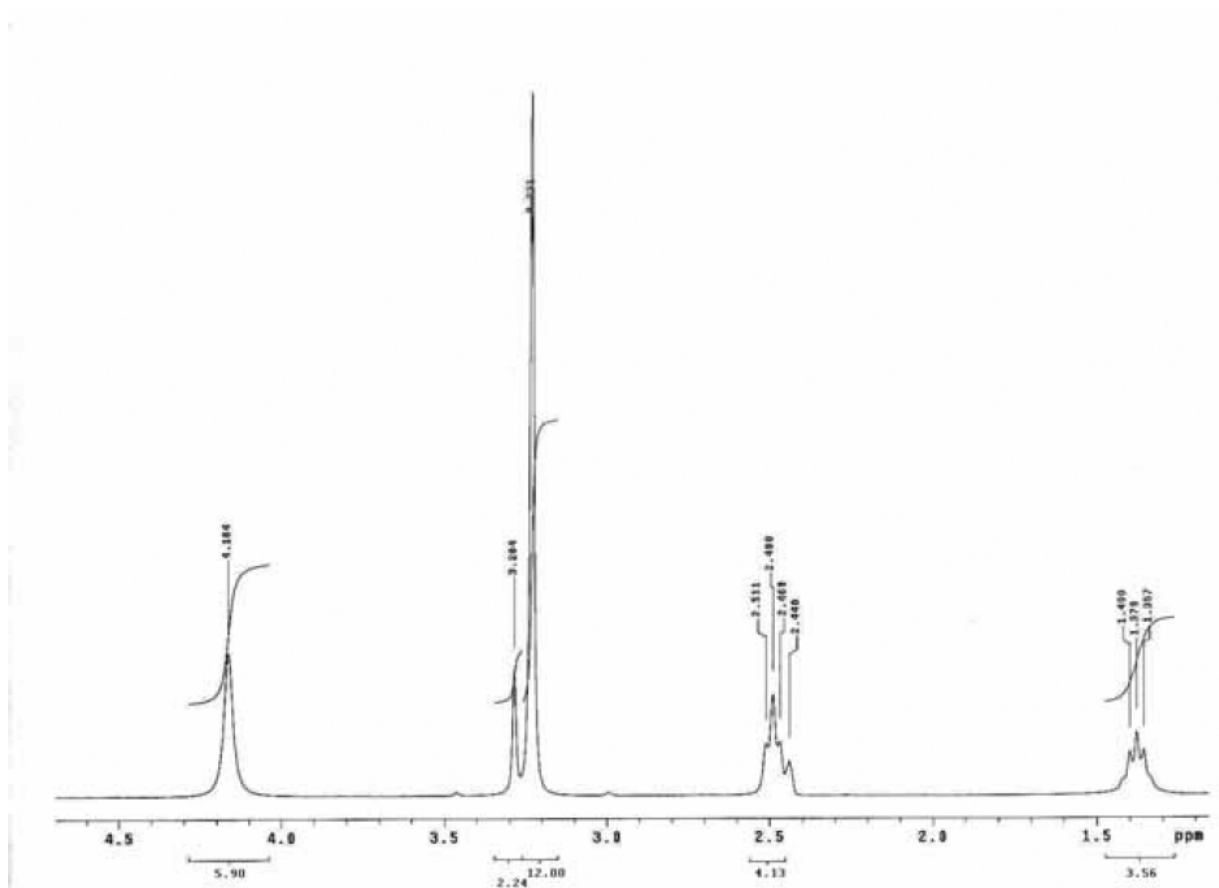


Fig.3S.  $^1\text{H}$  NMR spectrum of 0.07 M BTP in  $\text{DMSO-d}_6$

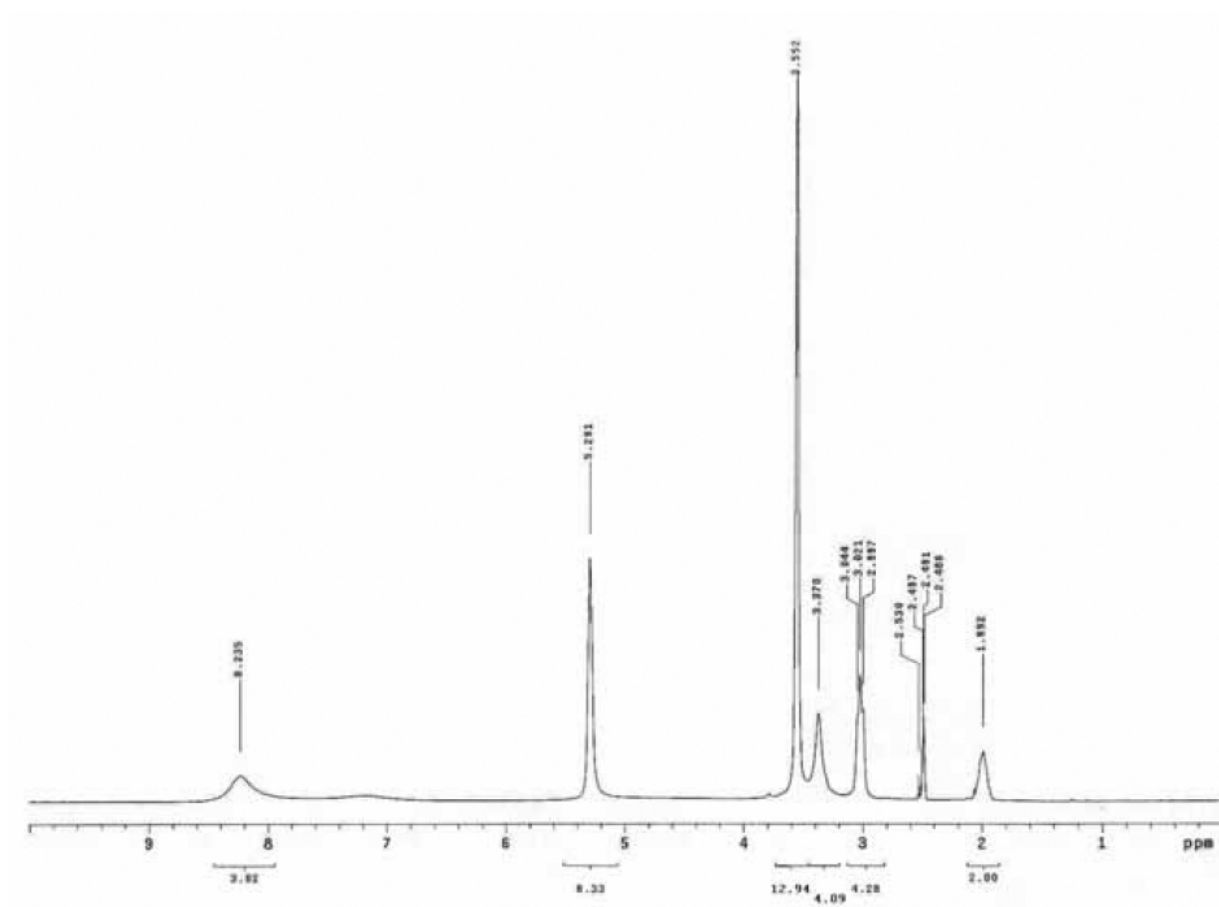


Fig.4S.  $^1\text{H}$  NMR spectrum of 0.04 M **2** in  $\text{DMSO-d}_6$

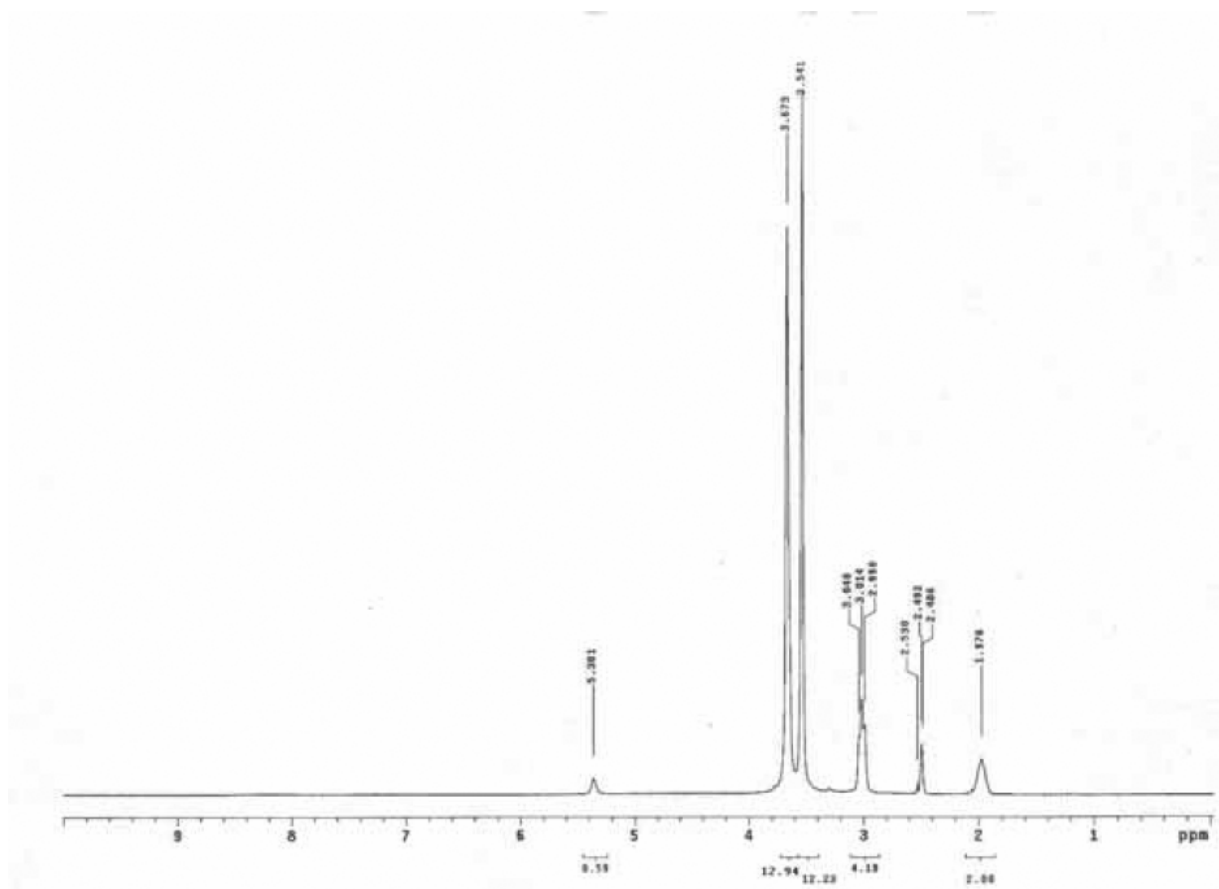


Fig.5S.  $^1\text{H}$  NMR spectrum of 0.04 M **2** in DMSO- $d_6$ /D $_2$ O 90/10

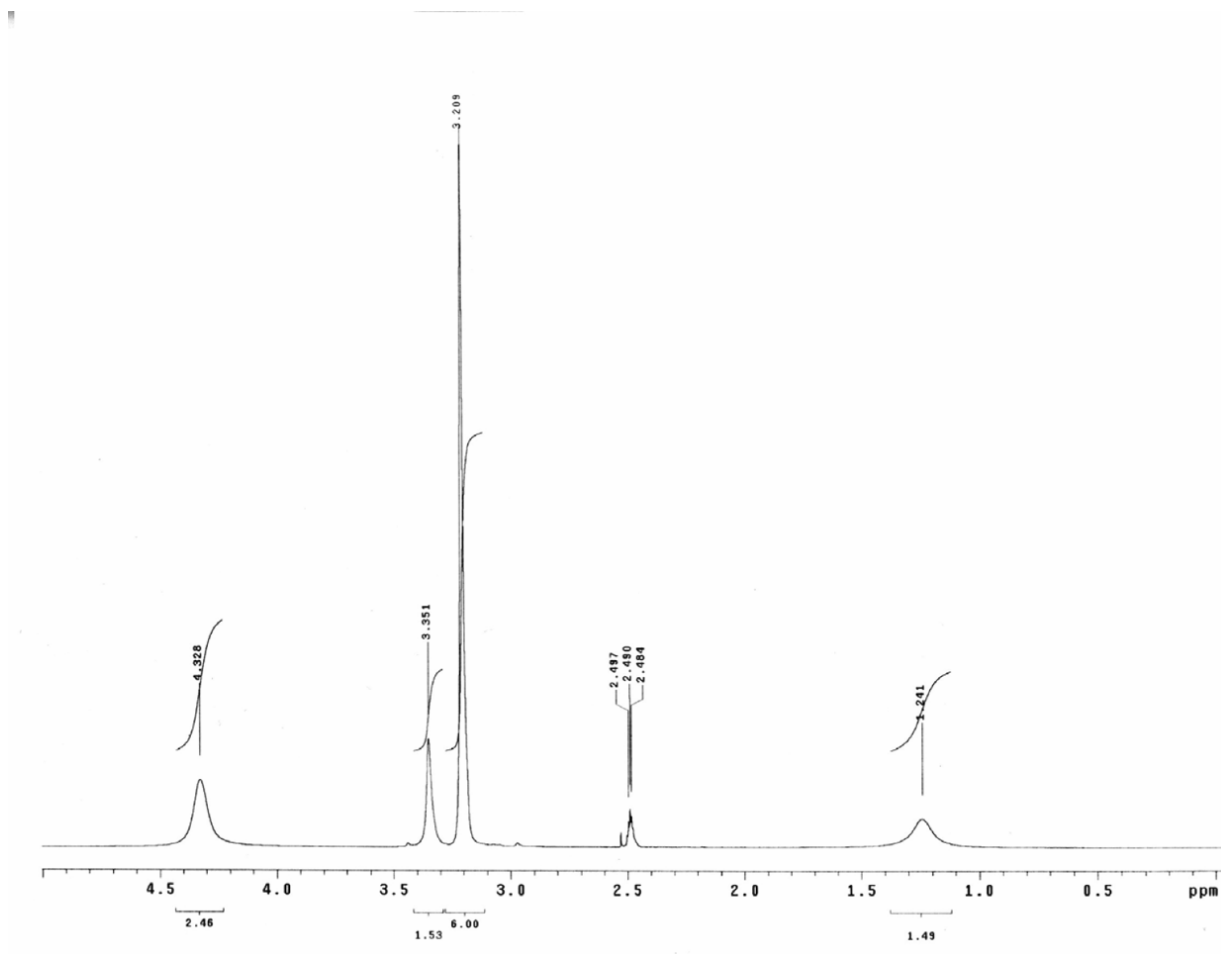


Fig.6S.  $^1\text{H}$  NMR spectrum of 0.05 M Tris in  $\text{DMSO-d}_6$

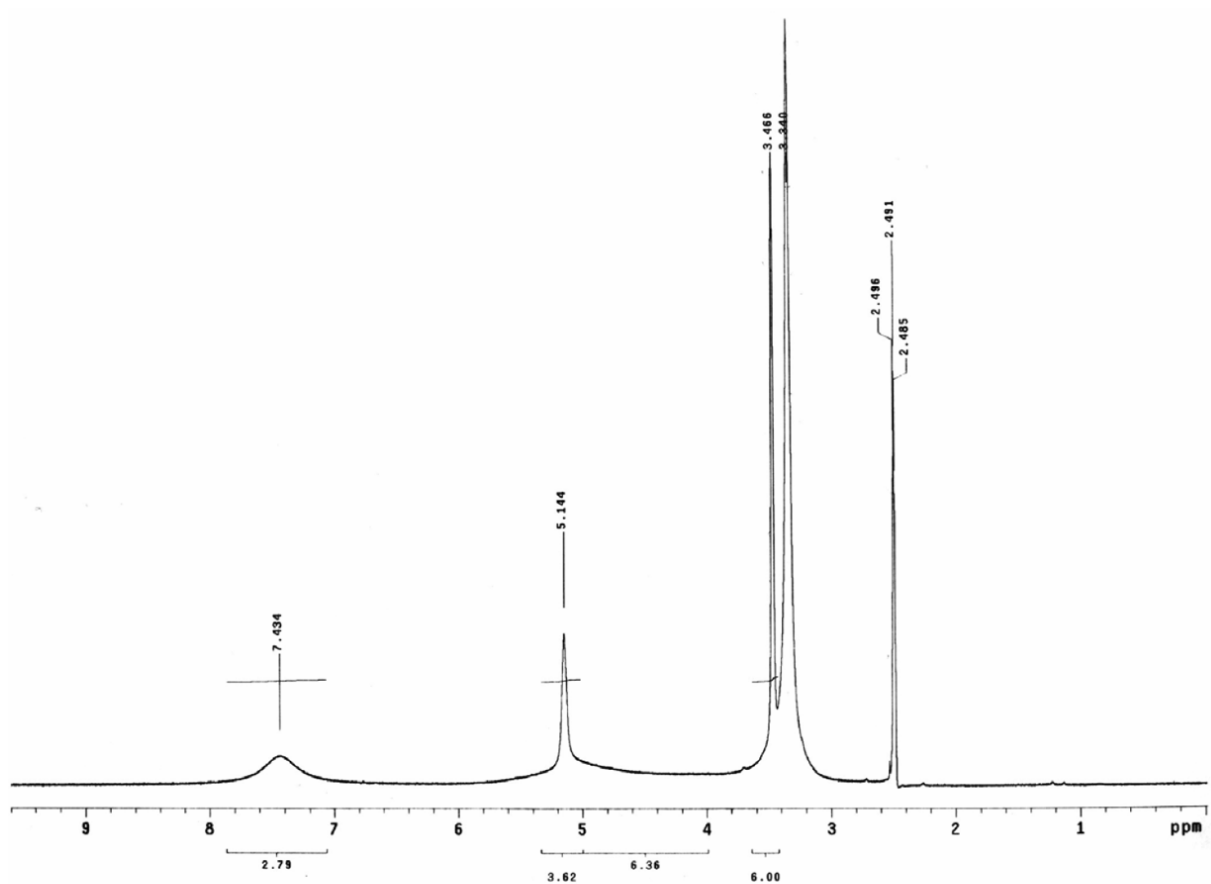


Fig.7S.  $^1\text{H}$  NMR spectrum of 0.02 M **3** in  $\text{DMSO-d}_6$

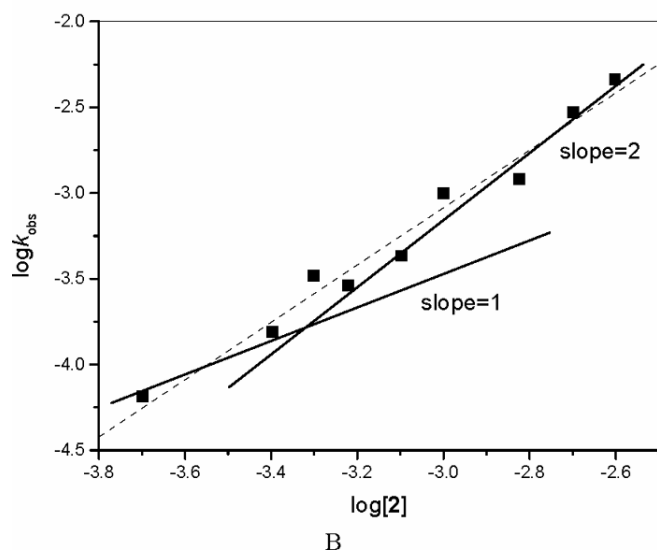
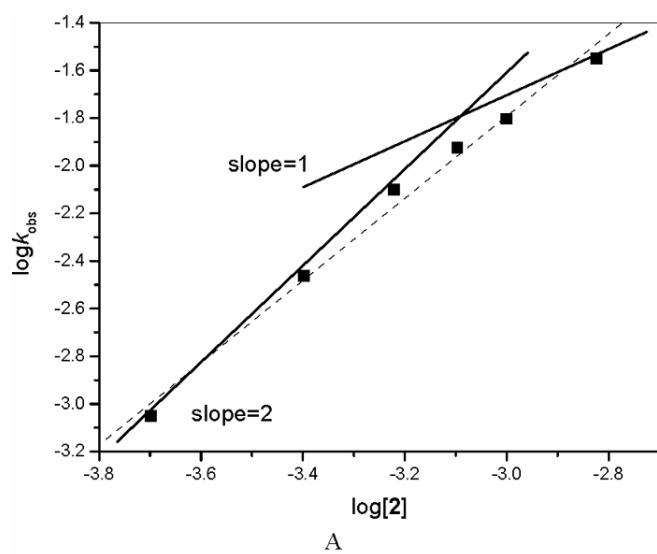
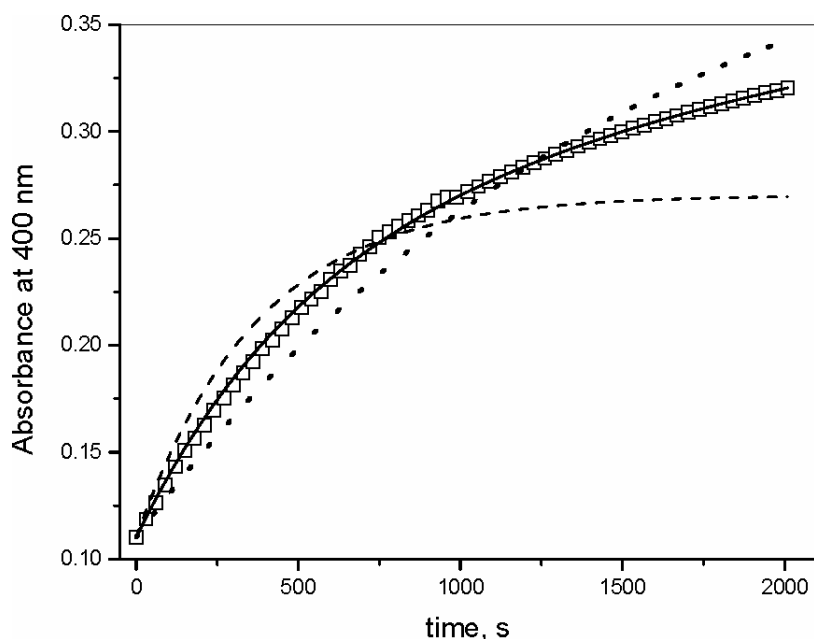


Fig.8S. Logarithmic plots of the observed first-order rate constants for the BNPP hydrolysis at 25°C vs. total concentration of **2** at pH 5.8 (A) and pH 7.9 (B).

The dashed lines show the linear fit with the slope 1.7 discussed in the text (see Fig.9). The solid lines have slopes 1 and 2 and illustrate that experimental points tend to approximate the slope 1 at higher concentrations of **2** at pH 5.8, but at pH 7.9 the tendency is opposite: at higher concentrations of **2** points follow the line with slope 2.





**Fig.9S.** The fitting of the kinetic curve for the hydrolysis of BNPP in the presence of 1 mM **2** at pH 6.9. The dashed line is the fit to first-order kinetics with liberation of only one *p*-nitrophenolate group (the hydrolysis of the diester proceeds much faster than subsequent hydrolysis of the monoester), the dotted line is the fit to first-order kinetics with simultaneous liberation of two *p*-nitrophenolate groups (hydrolysis of the monoester proceeds much faster than the hydrolysis of the diester), the solid line is the fit to the equation (1S) derived for the case when the hydrolyses of diester and monoester proceed with comparable rates. The initial absorbance at time 0 is due to the colour of the Ce(IV) solution.

The fitting results are:  $k_1=(1.97\pm 0.02)\times 10^{-3} \text{ s}^{-1}$  and  $k_2=(2.70\pm 0.05)\times 10^{-4} \text{ s}^{-1}$ . An independently measured first-order rate constant for the hydrolysis of *p*-nitrophenyl phosphate under the same conditions equals  $k_2=(3.21\pm 0.02)\times 10^{-4} \text{ s}^{-1}$ .

$$A = \varepsilon_{\text{NP}}[\text{BNPP}]_0 \left\{ 2 + \frac{(k_1 e^{-k_2 t} + (k_1 - 2k_2) e^{-k_1 t})}{(k_2 - k_1)} \right\} \quad (1S)$$